COMPLETE SPECIFICATION.

Process for the Catalytic Hydrogenation of Block Copolymers.

We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N.V., a Company organised under the laws of The Netherlands, of 30 Carel van Bylandtlaan, The Hague, The
5 Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
10 This invention relates to the catalytic hydrogenation of a block copolymer of a conjugated diene and a vinyl substituted aromatic hydrocarbon.

The older type of copolymers were random
15 copolymers wherein the two types of monomers are simultaneously copolymerized in such a way that the polymeric chain consisted of more or less random arrangements of the condensed monomeric units of both of the
20 monomer types mingled together. More recently, block copolymers have been synthesized by several different means resulting in at least two blocks but also including block copolymers of many alternating blocks where-
25 in each successive block in the copolymer chain comprises a different monomer from the polymer block preceding or following.

These copolymers show an undesirable oxidation and thermal sensitivity on the one
30 hand, and a relatively low service temperature on the other. The oxidation and thermal sensitivity is largely due to the conjugated diene portion, the relatively low service temperature to the vinyl arene content of the
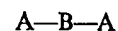35 block copolymer.

Certain efforts have been made to improve these properties, among which has been hydrogenation. Difficulties have been encountered, however, in the choice of hydro-
40 genation catalysts since it has been the previous experience that catalysts capable of

hydrogenating the polymers are relatively ineffective or, in other terms, exhibit low efficiency. This requires either excessive amounts of catalysts reaching uneconomic 45 levels in many cases or requiring unduly prolonged hydrogenation treatments. The latter necessity in itself constitutes a material disadvantage since the subjection of polymers to extended elevated temperatures 50 during hydrogenation normally causes extensive degradation of the polymer resulting in low molecular weight products.

Other disadvantages encountered when attempting to hydrogenate polymers with 55 prior art catalysts include lack of complete saturation even after extended hydrogenation periods, non-selective hydrogenation (when saturation of only certain types of linkages is desired) and low rate of hydrogenation and 60 difficulty of catalyst separation.

The invention provides a process for the catalytic hydrogenation of a block copolymer of a conjugated diene and a vinyl substituted aromatic hydrocarbon which comprises con- 65 tacting a solution of the polymer in an inert solvent with hydrogen in the presence of a catalyst comprising the reaction product of a cobalt, nickel, manganese, molybdenum, or tungsten metal compound and an aluminium 70 containing reducing agent.

The invention especially contemplates the hydrogenation of block copolymers having the general formula

$$A—B—A$$ 75

wherein each A is an independently selected polymer block of a vinyl substituted aromatic hydrocarbon and B is a polymer block of a conjugated diene, the conjugated diene con-

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tent being at least 65% by weight of the block copolymer.

Preferably, the block copolymers, prior to hydrogenation, are those in which the center polymer block is formed from a conjugated diene hydrocarbon having from 4—10 carbon atoms per molecule. The end blocks preferably have average molecular weights within the range between about 8000 and 60,000 while the center block of the conjugated diene has an average molecular weight of between about 50,000 and 300,000.

The catalysts utilized in the process of the present invention have several virtues not encountered in catalysts previously employed for the hydrogenation of elastomers or other polymers. In the first place, they are extremely active. Secondly, they exhibit a high efficiency; in other words, it is possible to employ remarkably low ratios of catalysts to polymer in the hydrogenation process. Thirdly, they are unexpectedly selective in that at relatively low hydrogenation temperatures, only the conjugated diene portions of the copolymers are fully hydrogenated while no more than about 25% or even less of the vinyl arene portions of the copolymers are converted. Finally, it is especially valuable to be able to control the specific location of hydrogenation, or, if desired, to hydrogenate substantially the whole of the copolymer chains merely by temperature control, all as more fully described hereinafter.

The catalysts employed in the process of the invention are compositions containing a reduced metal form of a member selected from the group consisting of cobalt, nickel, manganese, tungsten and molybdenum, as well as mixtures thereof, wherein said reduced metal form is obtained by reacting a compound of the above metals with an aluminium containing reducing agent. Suitable reducing agents include aluminium hydride and hydrocarbyl aluminium compounds of from 3—35 carbon atoms, especially trihydrocarbyl aluminium compounds of from 3—35 carbon atoms per molecule. The freshly reduced compositions may be prepared and used as hydrogenation catalysts in situ or may be separated prior to use. Ordinarily, moderate amounts of heat are employed to effect the reduction of the metal compounds, although heating is not required for catalyst formation. For convenience, temperatures of from 0° C to 250° C may be employed. Generally, temperatures of from room temperature to 225° C are suitable.

The ratio of reducing agent to reduceable metal compound may vary widely since even a partial reduction results in the production of an active hydrogenation catalyst. Molar ratios of reducing agent to reduceable metal compound of from 0.1:1 to 30:1 may be employed to produce the active hydrogenation catalyst compositions of the present invention. Molar ratios of from 0.5:1 to 10:1 are preferred.

The term " reduction " as it is used in the specification means the deposition of a metal in metallic or zero-valent form. This term includes the reduction of dicobalt octacarbonyl to metallic cobalt, even if the cobalt in dicobalt octacarbonyl is already in the zerovalent state.

Preparation of the hydrogenation catalysts with unusually high activity is accomplished by reacting the metal salt with an organoaluminium compound of the formula: $R_{3-n}AlX_n$ wherein R is a hydrocarbon group of from 1 to 10 carbon atoms, X is hydrogen or a halogen (chlorine, bromine, iodine, or fluorine) and n is an integer from 0 to 3, (preferably from 0 to 2) inclusive; n is 3 only when X is hydrogen, R may be an alkyl, aryl, alkaryl, aralkyl, or cycloaliphatic group. Examples of such groups include methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, sec.-butyl, tert.-butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, phenyl, benzyl, cumyl, tolyl, cyclopentyl, cyclohexyl, cyclohexenyl, and naphthyl radicals. When R is an alkyl group, lower alkyl radicals (1 to 4 carbon atoms) are preferred (methyl, ethyl, propyl, and butyl). Although n may be an integer from 0 to 2, inclusive, trihydrocarbyl aluminium compounds such as tri (lower alkyl) aluminium are preferred reducing compounds; in this preferred case n is zero. Tri(hydrocarbyl) aluminium compounds are also preferred because small amounts of halogen tend to poison the metallic hydrogenation catalysts formed according to the present invention.

Thus, in many respects the catalysts prepared for use in the process of the present invention have unique properties in addition to their high activity which make them especially valuable hydrogenation catalysts. Other metals of known hydrogenation ability did not respond to the procedure of the present invention and did not lead to catalysts of unusual hydrogenation activity. Manganese and molybdenum, however, which were previously thought to be too inactive to be useful for hydrogenation, are appreciably activated by the process of the present invention. Of the five metals, the specially prepared cobalt metal is the most active as a hydrogenation catalyst.

The catalysts produced according to the present invention may be prepared either in slurry form or mounted on a suitable support. The slurry form of the catalyst may be easily prepared by contacting the metal compound in an anhydrous solvent with the reducing agent in a dry, inert, atmosphere. When this procedure is followed, the solution turns black, heat is evolved, and a black deposit forms. For example, when a heptane solution of dicobalt octacarbonyl and tri-

alkylaluminium (or triphenyl-aluminium) are mixed in a dry nitrogen atmosphere a black slurry of reaction product is formed. The infra-red spectrum of the catalytic material so formed shows no metal carbonyl bonds. Magnetic susceptibility measurements show that the material is ferromagnetic, indicating the presence of cobalt metal.

Any metal compound may be used. Metal salts may be used as well as organometallic compounds and coordination complexes. Because of their relatively high cost, compounds such as dicobalt octacarbonyl and organometallic cobalt compounds are less desirable starting materials. Cobaltous salts are therefore preferred sources of metallic cobalt. Salts of organic or inorganic acids may be used. Salts of alkanoic acids with from 1 to 12 carbon atoms in the alkanoate moiety are particularly suitable. Dicobalt octacarbonyl, cobaltous acetate, cobaltous hydroxide (cobalt hydrate), and cobaltous octonate all give essentially the same results and are all converted by the organometallic reducing agent (such as a trialkylaluminium) to similar catalyst species. Thus, the catalytic activity of the metal is apparently independent of both the valence of the metal (prereduced, zero-valent state in metal octacarbonyl) and the source of the anion when a salt form is used. It is desirable to choose an inert solvent which dissolves the organo aluminium reducing agent. Metal salts (such as cobaltous chloride) which contain anions which tend to poison hydrogenation catalysts are, of course, less suitable for the preparation of the active catalyst because an extra step (removal of the toxicant) must be performed prior to use of the catalyst. Similarly, cobalt oxide, while it may also be used, does not form a catalyst with as high an activity.

While the previously defined organoaluminium compounds of the formula R_3-nAlX_n are prefered reducing agents for the formation of the metallic hydrogenation catalysts of the present invention, other aluminium-containing reducing agents may be employed. For example, aluminium powder may be used as well as lithium aluminium hydride and aluminium hydride (AlH_3). These materials, while yielding active catalysts, are not as efficient as the preferred tri(hydrocarbyl) aluminium reducing agents. Other organometallic and organometalloid reducing agents failed to produce the metallic cobalt (or mangenese, molybdenum, etc.) in activated form, even though these compounds reduced cobalt compounds to cobalt metal.

Since the catalysts are readily formed in situ, it is convenient to dissolve (or mix) one of the components, e.g., a cobalt salt, in polymer cement and thereafter add a hydrocarbon solution of the reducing agent thereto.

The polymers to be hydrogenated are dissolved in a suitable solvent therefor or in mixtures of solvents. Unsaturated solvents such as benzene or toluene may be employed, but it will be understood that such solvents may be hydrogenated prior to or during the course of the following hydrogenation process. Consequently, it is more preferred to utilize polymers in the form of solutions of saturated solvents such as cyclohexane, mixtures of cyclohexane with hydrocarbons such as iso-octane, neopentane 2,4-dimethyl hexane and the like. Hydrogenation is normally conducted in an autoclave at hydrogen pressures between ambient pressure and about 3000 psig.

In one aspect of the process under consideration, it is possible to selectively hydrogenate the subject copolymers at temperatures below about 150° C with the above-described class of hydrogenation catalysts whereby at least about 90% of the diene units of the copolymer are saturated at the same time. Hydrogenation is more selective as the temperature is reduced, but of course, hydrogenation time is correspondingly extended as the temperature is reduced. Consequently, temperatures between about 25 and 150° C are preferred for this selective type of hydrogenation.

If hydrogenation of at least 75% of the vinyl arene units is desired, it is desirable to conduct the hydrogenation in two stages. When hydrogenation of this degree is the objective, it is possible to utilize temperatures up to about 175° C for the hydrogenation of the diene portion of the copolymer. At such temperatures, the hydrogenation of the diene portion of the copolymers is substantially complete, but the hydrogenation of the vinyl arene components rarely reaches more than about 25—35% of theoretical under these conditions. Thereafter the hydrogenation is continued at a temperature in excess of 175° C, but below the temperature at which substantial degradation of the copolymer occurs. In such a two-stage process the hydrogenation suitably passes rapidly through the lower temperature stage to the higher temperature stage with such speed that the diene linkages are hydrogenated before any substantial amount of thermal degradation occurs.

The time required for hydrogenation will depend not only upon the catalyst concentration relative to polymer, but also upon the extent of hydrogenation desired and the temperature at which the single or dual stages are conducted. Generally, the period of hydrogenation at temperatures below about 175° C when the conjugated diene portion of the copolymer is substantially completely hydrogenated, will be between about 0.05 and about 8 hours, while between about 0.5 and about 24 hours, are required for hydrogenation of more than about 90% of the vinyl arene portions of the copolymer

at the elevated temperatures described here-inbefore.

One of the features of the present invention comprises the discovery that the special catalyst forming an essential part of the hydrogenation system agglomerates during the elevated temperature period sufficiently that it can be readily removed from the hydrogenation mixture. Simple settling by means of gravity is possible when the concentration of the polymer is less than about 12% by weight of the total mixture or centrifuging may be employed if desired. It is not necessary (in contrast to experience with other hydrogenation catalysts) to further dilute the solution with fresh solvent nor to subject it to an extra heating period to cause such agglomeration. Of course, if the hydrogenation is only conducted at the temperatures below about 150° C for the hydrogenation of the diene portions only of the copolymer, then it may be necessary to heat for a period of 10 minutes—4 hours at temperatures in the order of 175—250° C in the absence of hydrogen in order to agglomerate the catalyst. This is not an essential feature, however, since the catalyst is in such a physical condition that it can be removed by filtration or other means.

Following completion of the desired degree of hydrogenation, the next stage is to isolate the polymer or to utilize the hydrogenated polymer in its cement form as it comes from the autoclave, preferably (but not necessarily) after removing the catalyst. For example, the cement may be converted into a latex by the addition of soap and water and eventual removal of polymer solvent under suitable conditions for latex formation. Alternatively, the cements may be laid down as a film; may be drawn as a fibre (both with suitable solvent removal stages) or may be coagulated by means of hot water and/or steam to recover the hydrogenated polymer in crumb form. Carbon black or other pigments may be incorporated in the hydrogenated polymer either prior to or subsequent to solvent removal. Antioxidants or thermal stabilizers, principally aromatic amines or phenols, may be added to the system following hydrogenation. The product may be combined with resins and tackifiers to form adhesive compositions or may be utilized for the formation of moulded objects.

The following examples illustrate preferred means for carrying out the process of the present invention.

EXAMPLES I—VI

A number of hydrogenations were carried out utilizing a block copolymer having the structure

polystyrene-polyisoprene-polystyrene

the block molecular weights in thousands being 15—80—15. This block copolymer had an intrinsic viscosity of 0.88 dl/g. For the purpose of hydrogenation, it was utilized as a cyclohexane cement containing 7% by weight of the polymer. The catalyst employed was used in slurry form and was cobalt acetate reduced with aluminium triethyl, the ratio of aluminium to cobalt being as given in the Table. The first stage of hydrogenation, which was carried out at 800 lbs. pressure in an autoclave, was 160° C in all cases. The Table gives the details of the hydrogenation, including the time of hydrogenation both in the first stage and in the second stage, the temperatures utilized in the second stage being given in the Table as well as the time. Catalyst concentration was varied as shown in the Table and the percent conversion of both diene units and of styrene units is included for each example. It will be noted that in hydrogenating according to Example I, at 160° C, both in the first and second stages, the diene portion of the copolymer was substantially completely converted while the styrene portion was converted only to the extent of about 25%.

In the succeeding examples, the second stage temperature was increased sufficiently to permit a high degree of conversion of styrene even though at the same time the catalyst concentration was radically reduced.

TABLE
2-Stage Hydrogenation of Block Copolymer

	Example					
	1	2	3	4	5	6
First temp. stage, °C	160	160	160	160	160	160
time, hr...	0.2	0.2	0.2	0.2	0.2	0.2
Second temp. stage, °C	160	210	210	210	225	245
time, hr.	2	1.4	3.2	7	2	1.5
g. Co/g. polymer	0.04	0.04	0.01	0.005	0.005	0.005
% Diene hydrogenation	~100	~100	~100	~100	~100	~100
% Styrene hydrogenation	25	99	96	92	98	99
I.V. of product dl/g	—	1.32	1.29	1.27	1.13	1.03
Al : Co ratio	2 : 1	2 : 1	2 : 1	3 : 1	3 : 1	3 : 1

EXAMPLE VII

In order to demonstrate the relative effectiveness of the catalysts of this invention in comparison with prior art polymer hydrogenation catalysts, the following comparative experiments were made: A block copolymer having the structure polystyrene-polyisoprene-polystyrene and having an iodine number of about 270 was hydrogenated in cyclohexane solution using a prior art catalyst, namely, nickel deposited on Kieselguhr (which is indicated by the literature to be the best known polymer hydrogenation catalyst) and a catalyst of the present invention in slurry form, namely cobalt octoate reduced with two mols of aluminium triethyl per mol of octoate.

The course of hydrogenation was followed by iodine number for diene double bonds and ultra-violet analysis for styrene content. Hydrogenation was conducted at about 500 psig H_2 pressure at about 155° C for both polyisoprene segments and polystyrene segments. After about 4 hours the sample containing 0.27 g nickel per g of polymer still had an iodine number of about 60, while the styrene segments were virtually unaltered. After 3/4 hours, the sample catalyzed with 0.01 g cobalt per gram of polymer on the other hand, showed substantially complete hydrogenation of the double bonds and 63% saturation of the styrene segments.

EXAMPLE VIII

The conditions of Example I were repeated using the same block polymer utilizing a catalyst in slurry form comprising the product of nickel acetyl-acetonate reduced with aluminium triethyl. After two hours hydrogenation at 160° C, all of the diene linkages had been reduced and 16% of the styrene had been hydrogenated.

EXAMPLE IX

The above example was repeated, replacing one-half of the cobalt salt with nickel acetylacetonate. After two hours, all of the diene unsaturation had been reduced, as well as 31% of the styrene unsaturation.

EXAMPLE X—XI

In order to test the effect of supports, the reduced catalyst compositions were formed on a diatomaceous earth filter aid. The following table gives the hydrogenation conditions and the results obtained by hydrogenation of the same block polymer used in Examples 1—6:

	Example	
	11	12
	Catalyst	
	1 mol cobalt acetate : 2 mols Al triethyl	1 mol nickel acetate: 2 mols Al triethyl
Hydrogen pressure, psi	500	500
Time, minutes	210	90
Temperature, °C	155	155
Ratio of metal to polymer, %	2	2
% diene linkages hydrogenated	98	99
% styrene hydrogenated	53	12

WHAT WE CLAIM IS:—

1. A process for the catalytic hydrogenation of a block copolymer of a conjugated diene and a vinyl substituted aromatic hydrocarbon which comprises contacting a solution of the polymer in an inert solvent with hydrogen in the presence of a catalyst comprising the reaction product of a cobalt, nickel, manganese, molybdenum, or tungsten metal compound and an aluminium containing reducing agent.

2. A process as claimed in claim 1, in which the polymer has the general formula A—B—A in which each A is an independently selected polymer block of a vinyl substituted aromatic hydrocarbon and B is a polymer block of a conjugated diene, the conjugated diene content being at least 65% by weight of the block copolymer.

3. A process as claimed in claim 2, in which the polymer blocks A have an average molecular weight between 8000 and 60,000 and the polymer block B has an average molecular weight between 50,000 and 300,000.

4. A process as claimed in any of the preceding claims, in which the aluminium containing reducing agent has the general formula $R_{3-n}AlX_n$ in which R is a hydrocarbyl radical having from 1 to 10 carbon atoms, X is hydrogen or halogen and n is an integer from 0 to 3, with the proviso that if n = 3, X is hydrogen.

5. A process as claimed in claim 4, in which n is an integer from 0 to 2.

6. A process as claimed in claim 5, in which n is zero.

7. A process as claimed in any of claims 4 to 6, in which R is an alkyl radical having from 1 to 4 carbon atoms.

8. A process as claimed in any of the preceding claims, in which in the catalyst the molar ratio between the aluminium containing reducing agent and the metal compound is between 0.1 : 1 to 30 : 1.

9. A process as claimed in claim 8, in which said molar ratio is between 0.5 : 1 and 10 : 1.

10. A process as claimed in any of the preceding claims, in which in the catalyst the metal compound is a cobalt compound.

11. A process as claimed in any of the preceding claims, in which the conjugated diene polymer block of the block copolymer is selectively hydrogenated at a temperature between 25° C and 150° C.

12. A process as claimed in claim 1 substantially as described in any of the Examples.

13. A hydrogenated block copolymer whenever obtained by a process as claimed in any of the preceding claims.

14. A process for the manufacture of articles in which a hydrogenated block copolymer as claimed in claim 13 is formed into an article.

15. Articles manufactured by a process as claimed in claim 14.

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